

it gives rise to terms with $(\vec{Q} \cdot \vec{Q}')$, $(Q^2 + Q'^2)\vec{Q} \cdot \vec{Q}'$, $(\vec{Q} \cdot \vec{Q}')^2$, and $Q^2 Q'^2$, because Γ should vanish at the long-wavelength limit. This kind of treatment is valid in insulating ferromagnets, where we have a $T^{5/2}$ dependence of D . However, there is no reason for Γ to be an integral function of Q and Q' . As shown in Eq. (9), our interaction leading to a T^2 dependence of D is not an integral function of Q and Q' , while it still vanishes at the long-wavelength limit as required. Note that the third derivative of Eq. (9) is not continuous at $Q' = Q$. The appearance of such a singular interaction is due to the continuum of electron states outside the Fermi surface.

We note finally the approximate nature of the present treatment. The starting point of the treatment is a Hartree-Fock solution, which is based on the neglect of the Coulomb correlation. The correlation acts in such a way that electron interactions are screened. If one could interpret our V to be an effective interaction with an appropriate screening effect, the present theory might still work, if the frequency dependence of the effective interaction is assumed to be negligible. It is a difficult problem to determine the change of magnitude of magnon interactions in the theory with the screening effect taken into account self-consistently.

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SIGN OF THE CONDUCTION ELECTRON CONTRIBUTION TO THE ELECTRIC FIELD GRADIENT IN METALS*

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Thus far, the magnitude of the nuclear quadrupole coupling has been determined in about a dozen metals by magnetic resonance (including "pure quadrupole" resonance) and specific-heat measurements. These measurements do not, however, determine the sign of the interaction which is of considerable importance from the standpoint of determining whether the two contributions to the total interaction—that due to the lattice of point charges and that due to the conduction electron distribution—have the same or opposite sign. This follows from the fact that the lattice contribution can be calculated with considerable confidence,^{1,2} and although its actual magnitude depends on the Sternheimer antishielding factor,³ its sign does not. On the other hand, the con-

duction electron contribution has not been considered readily amenable to calculation,^{4,5} and the magnitude of the measured total interaction must be used, together with the calculated lattice contribution, to estimate this quantity. The purpose of the present note is to point out evidence for the lattice and conduction electron contributions having opposite sign in the case of pure β -tin, and to suggest possible correlation between the conduction electron contribution and the anisotropic Knight shift⁶ in metals.

Evidence for the difference in sign is based on recent Mössbauer effect measurements of the magnitude and sign of the quadrupole coupling of the first excited nuclear level of ¹¹⁹Sn in metallic tin and on a value for the quadrupole moment

of the first excited level, $Q(^{119m}\text{Sn})$, derived from Mössbauer effect measurements on nonmetallic tin compounds. Alekseevskii et al.⁷ measured the magnitude and sign of the quadrupole splitting in single crystals of β -tin. They found the interaction to be negative and to have the magnitudes

$$\begin{aligned} \left| \frac{1}{2} e^2 q_{zz} Q/h \right| &= 8.8 \pm 4 \text{ Mc/sec at } 298^\circ \text{K}, \\ &= 9.6 \pm 4 \text{ Mc/sec at } 77^\circ \text{K}. \end{aligned}$$

Boyle et al.⁸ measured the ^{119m}Sn quadrupole splitting in powdered tetragonal SnO and were able to determine the sign of the coupling from the asymmetry of the spectrum. From the calculation of the sign and magnitude of the field gradient (due to covalent bond electrons) they derived

$$Q(^{119m}\text{Sn}) = -0.08 \pm 0.04 \text{ barn}.$$

With this value of the quadrupole moment, we can infer that the total electric field gradient (EFG) in β -tin has the value

$$eq_{\text{exp}}(\beta\text{-tin}) = +3000 \times 10^{12} \text{ esu } (\pm 50\%).$$

The EFG at the ^{119m}Sn site may be considered to consist of two contributions, eq_{cond} and $eq_{\text{latt}}(1 - \gamma_\infty)$. Here, eq_{cond} is due to the non-spherical distribution of the conduction electrons inside the central atomic cell whereas eq_{latt} is due to the external charges of the ion cores shielded by a uniform distribution of the conduction electrons. The factor $(1 - \gamma_\infty)$ gives the Sternheimer antishielding enhancement³ of the lattice contribution, with the latter quantity itself given by²

$$eq_{\text{latt}} = -\frac{Ze}{V} \int \frac{2P_2(\cos\theta)}{r^3} d^3r + Ze \sum_L \frac{2P_2(\cos\theta)}{r_L^3}. \quad (1)$$

We have calculated eq_{latt} for the case of β -tin using the plane-wise summation method developed by de Wette,² considering the tin lattice as made up of four interpenetrating simple tetragonal lattices centered, respectively, at $(0, 0, 0)$; $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$; $(\frac{1}{2}, 0, \frac{3}{4})$; $(0, \frac{1}{2}, \frac{1}{4})$, and taking the lattice constants as $c = 3.1749 \text{ \AA}$ and $a = 5.8197 \text{ \AA}$. The result obtained is that

$$eq_{\text{latt}}(\beta\text{-tin}) = -1.67 \times 10^{13} \text{ esu}.$$

On the basis of a calculation of γ_∞ for In^{3+} ,⁹ we estimate that for Sn^{4+} , $\gamma_\infty = -10$. With this,

$$eq_{\text{latt}}(1 - \gamma_\infty) = -183 \times 10^{12} \text{ esu}.$$

Comparison of this result with the experimental total EFG shows that in order to account for the experimental EFG we need to assume that the contribution due to the conduction electrons in the central cell is an order of magnitude larger than and of opposite sign to the lattice contribution. That is, we need

$$eq_{\text{cond}} \approx +3200 \times 10^{12} \text{ esu}.$$

The sign of eq_{cond} is the same as that of the Knight shift anisotropy in β -tin.⁵ We have re-measured this latter quantity and find that

$$(\Delta H_{\parallel} - \Delta H_{\perp})/H_0 = 3K_{\text{ax}} = +0.075\%.$$

The Knight shift is defined by⁶

$$K_{\text{ax}} = \beta^2 V_c N(E_{\text{F}}) q_{\text{F}},$$

where β is the Bohr magneton, V_c is the atomic volume, $N(E_{\text{F}})$ is the one-electron density of states per unit energy and volume, and the quantity q_{F} is defined by

$$q_{\text{F}} = \left\langle \int_{\text{atomic volume}} \psi_k^*(\vec{r}) \left(\frac{3\cos^2\theta_k - 1}{r^3} \right) \psi(\vec{r}) d^3r \right\rangle_{\text{F}} \quad (3)$$

where the average is over the Fermi surface, and θ_k is the angle between H_0 and the radius vector connecting the electron and the nucleus. Thus, q_{F} measures the average quadrupole moment per electron at the Fermi surface.

On the other hand, the contribution of the conduction electrons in the central cell to the EFG, eq_{cond} , can be expressed as

$$eq_{\text{cond}} = \left\langle \int_{\text{atomic volume}} \rho(\vec{r}) \left(\frac{3\cos^2\theta - 1}{r^3} \right) d^3r \right\rangle_{k \leq k_{\text{F}}}, \quad (4)$$

where the average is now over the entire occupied conduction band, and $\rho(\vec{r}) = Ze \psi_k^*(\vec{r}) \psi_k(\vec{r})$. Using the very simple approximation for the wave function that

$$\psi_k(\vec{r}) = u_0(\vec{r}) \exp(i\vec{k} \cdot \vec{r}),$$

where $u_0(\vec{r})$ is the wave function at the bottom of the conduction band, the two averages per unit cell are the same:

$$Zeq_{\text{F}} = eq_{\text{cond}}. \quad (5)$$

We have calculated the value of Zeq_{F} for the metals Sn, In, and Sc using the relation (2). The

Table I. Values of the electronic specific heat γ , density of states $N(E_F)$, anisotropic Knight shift K_{ax} , nuclear quadrupole moment Q , experimental quadrupole coupling e^2qQ/h , and the lattice field gradient $eq_{latt}(1-\gamma_\infty)$, for the metals scandium, indium, and tin.

Metal	γ (10^{-3} J/mole-deg ²)	$V_c N(E_F)$ (10^{12} cgs)	K_{ax} (%)	Q (10^{-24} cm ²)	$ e^2qQ/h $ (Mc/sec)	$eq_{latt}(1-\gamma_\infty)$ (10^{12} cgs)
Sn	1.80 ^a	0.47	+0.0235	-0.08 ^e	17.66 ^h	-183
In	1.61 ^a	0.43	-0.14 ^c	+1.16 ^f	29.54 ^c	- 81.7 ⁱ
Sc	11.3 ^b	3.00	-0.03 ^d	-0.22 ^g	2.15 ^d	+ 60 ^j

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ⁱReference 2.

^jReference 1.

values of $V_c N(E_F)$, as well as the values of the electronic specific heat γ on which these are based, and of K_{ax} are listed in Table I. Table I also lists the values of the experimental quadrupole coupling in these metals and the values of the lattice contribution to the EFG that were used to derive the conduction electron contribution, eq_{cond} . In the cases of In and Sc we have taken the sign of eq_{exp} to be that which makes the sign of eq_{cond} the same as that of eq_F . Finally, we show in Table II the comparison between the two quantities that, according to (5), should be equal.

As is clear from the entries in Table II, the agreement between Zeq_F and eq_{cond} is relatively poor. This disagreement is, however, to be expected since we have very simply assumed that

Table II. Comparison of the conduction electron contribution to the total EFG calculated from the anisotropic Knight shift, Zeq_F , and the conduction electron contribution deduced from the measured total quadrupole coupling and the calculated lattice contribution. In the cases of indium and scandium the sign of the measured coupling has been chosen so as to give the sign of the electronic contribution in agreement with the sign of the Knight shift anisotropy.

Metal	Zeq_F (cgs)	$eq_{cond} = eq_{exp} + eq_{latt}(1-\gamma_\infty)$
Sn	$+11\,170 \times 10^{12}$	$+3200 \times 10^{12} (\pm 50\%)$
In	$-54\,500 \times 10^{12}$	-270×10^{12}
Sc	-1581×10^{12}	-195×10^{12}

the average quadrupole moment per conduction electron at the Fermi surface is the same as the average quadrupole moment over the entire conduction band. However, in all cases the discrepancy is in the right direction, since we should expect that the non-s character of the conduction electron wave functions at the Fermi surface will be greater than the average non-s character over the whole band.

Another source of overestimation of Zeq_F can be due to a possible contribution to K_{ax} resulting from g -factor anisotropy.⁶ This adds to the right side of (2) a contribution $(g_{||} - g_{\perp})K_{iso}/g_0$, where K_{iso} is the isotropic Knight shift. For white tin, such a contribution appears to be negligible according to an observed g -factor anisotropy of roughly¹⁰

$$(g_{||} - g_{\perp})/g_0 \approx 0.0014$$

which gives for a contribution to $3K_{ax}$ only $\sim 0.001\%$ compared to the experimental value of 0.07% .

In conclusion, we have shown that for β -tin the lattice and conduction electron contributions to the EFG are of opposite sign and that the sign of eq_{cond} is the same as that of eq_F . Furthermore, the value of K_{ax} , and hence of q_F , appears helpful in establishing the sign and an upper limit for eq_{cond} . More realistic approximations for ψ_k and the band structure will be needed in order to achieve better quantitative agreement between eq_F and eq_{cond} .

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EFFECT OF THE Fe³⁺-Tm³⁺ EXCHANGE INTERACTIONS ON THE PARAMAGNETIC RESONANCE AND RELAXATION OF IRON IMPURITIES IN THE THULIUM GARNETS

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In a recent Letter Hutchings and Wolf¹ have reported on the paramagnetic resonance of Yb³⁺ impurities in thulium aluminum (TmAlG) and thulium gallium (TmGaG) garnets. The Tm³⁺ ion's lowest multiplet, $4f^{12}H_6$, has in these crystals a singlet ground state² separated from the next excited state by 30 to 60 cm⁻¹. Therefore, at sufficiently low temperatures these two garnets will behave similarly to their diamagnetic counterparts, and permit the observation of paramagnetic resonance of other impurities. As indicated in reference 1, such resonances will exhibit effects due to exchange interactions between the impurity and the neighboring Tm³⁺ ions. The parameters of the spin Hamiltonian that describes the electron paramagnetic resonance (EPR) spectrum of the impurity will have contributions arising from the exchange interactions. The structure constants exhibit significant variations between the various garnets, and so do the spin-Hamiltonian parameters for most impurities. In reference 1 the exchange contribution to the g tensor of Yb³⁺ in the Tm garnets was isolated by comparing the g values measured in these with values obtained by interpolation for a hypothetical diamagnetic host with the same structure as the Tm garnet. Such a procedure gives acceptable results because the variations in the g values in the diamagnetic garnets are smooth functions of the structural parameters.

The ⁶S ground state of Fe³⁺ has, in most diamagnetic hosts, an isotropic g tensor, with a g value essentially equal to that of a free spin. Any

exchange contributions to it can therefore be immediately isolated. Exchange contributions to the other spin-Hamiltonian parameters of Fe³⁺ in the Tm garnets are also expected and may be isolated by the interpolation procedure of reference 1. In addition, the Fe³⁺-Tm³⁺ exchange interactions may bring about³ a two-phonon spin-lattice relaxation process for Fe³⁺ involving lattice oscillators with energy essentially equal to the Tm³⁺ crystal field splitting. This effect would appear as an exponential temperature dependence governing the Fe³⁺ relaxation, having an activation energy equal to the Tm³⁺ splitting.

A study of the Fe³⁺ EPR spectrum and relaxation in a series of garnet hosts has indeed revealed the presence of all above mentioned effects in TmGaG and TmAlG.

There are two chemically inequivalent sites available for the Fe³⁺ impurities. For dilute solutions in the gallium garnets a strong preferential substitution at the a (octahedral) sites is observed⁴; the concentrations of Fe³⁺ at the a and d (tetrahedral) sites are about equal in the Al garnets. Consequently, in TmGaG we were not able to detect any lines that could, with certainty, be ascribed to Fe³⁺ in d sites. A complete octahedral Fe³⁺ spectrum was observed in all crystals. It is qualitatively similar for all samples including that of the Tm garnets. Complete tetrahedral spectra were only found (with the available frequencies and field range) in the diamagnetic hosts. However, we did observe a set of lines in TmAlG which exhibit tetrahedral